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ON THE RAMAN SPECTRA OF A FEW ALIPHATIC KETONES AT LOW TEMPERATURES

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(Plate II)

ABSTRACT. The Raman spectra of acetone, diethyl, methyl-ethyl-and di-*n*-propyl ketone have been studied in the solid state at about $-170°C$ and in the liquid state at the room temperature. The polarisation of the Raman lines in the liquid state has also been studied. It is observed that some of the prominent Raman lines undergo changes in position and intensity with the solidification of the substances at the low temperature. The line 1705 cm.$^{-1}$ due to the oscillation of the C=O group seems to be diminished in intensity in the solid state in the case of acetone, diethyl ketone and di-*n*-propyl ketone. A new line is observed in the low frequency region in each of the spectra of solid methyl, ethyl and diethyl ketone. These results have been discussed.

INTRODUCTION

The Raman spectra of a few aliphatic sulphides were studied previously in the solid state at low temperatures by the present authors (Sirkar & Bishui, 1943) and it was observed that some of the Raman lines undergo changes in frequency and intensity with the solidification of the substances at low temperatures. These changes indicate distortion of the molecules and in some cases probably formation of secondary association bonds between them, giving new lines in the low frequency region. The alternative explanation regarding the origin of the new lines in the low frequency region is that they are due to some types of lattice oscillations in which only electrostatic intermolecular field is involved. If this second explanation be correct it is expected that molecules having similar structure would give similar lines in the low frequency region in the solid state. In order to elucidate this point the investigations have been extended to four aliphatic ketones, the molecules of two of which are similar to those of two of the sulphides studied earlier, with the only difference that the sulphur atom of the sulphides is replaced by the C=O group. These results are discussed in the present paper.

EXPERIMENTAL

The technique used in the present investigation for studying the Raman spectra of the substances at the low temperatures is the same as employed in the previous investigation (Sirkar & Bishui, 1943). The substances studied are acetone, diethyl, methyl ethyl and di-*n*-propyl ketone. All these liquids were obtained from Kahlbaum's original bottles and redistilled in vacuum. The

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polarisation of the Raman lines due to the liquids have been studied by photographing the horizontal and vertical components simultaneously with the help of a double-image prism. The Fuess spectrograph used in the investigation gave a coma extending upto about 38 cm^{-1} on the Stokes side of 4046 A. U., and therefore the presence of any new Raman line with a lower frequency shift could not be detected. Inspite of the special care taken to solidify the substances slowly in order to obtain a homogeneous transparent mass, the spectrum of the scattered light showed the presence of strong continuous background due to extraneous light, and therefore it has not been possible to record all the faint Raman lines in the solid state. The spectrogram due to solid acetone, however was found to be quite satisfactory. For these reasons no special care has been taken to record all the faint Raman lines in the liquid state of these substances.

RESULTS AND DISCUSSION

The results are given in Table I-IV. The polarisation of the lines is indicated by the letter P and total depolarisation by D. The approximate intensities are given in parentheses. The lines in the low frequency region ($\Delta \nu < 120$ cm^{-1}) and those with higher frequencies are discussed separately in the following paragraphs.

TABLE I

Acetone

Liquid at about 30°C		Solid at about −170°C Present authors
Previous authors	Present authors	
392 (2) D	392 (1) e; D	95 (ob) k ?
487 (½) ?	487 (0) e ?	
527 (2) P	528 (3) e, k; D	
789 (5) P	790 (8) e, k; P	800 (3) e, k
903 (0) ?	903 (0) e, k; P	
1065 (1) P	1065 (1) e, k; P	1062 (0) e, k
	1222 (2) k; D	
1221 (1) D	1358 (0) k; P	
1358 (0) P	1423 (4b) e, k; D	1430 (1) e, k
1423 (3b) D	1705 (5) e; P	1702 (1) e
1705 (5) P		
2689 (0) ?	2690 (0) e, k; P	
2857 (ob) ?	2857 (2b) e, k; P	
2923 (10) P	2923 (10) e, k; P	2925 (5) e, k
2964 (4) —	2964 (3) e, k; D	2976 (3) e, [k]
3006 (4) —	3006 (3) e, k; D	3008 (3) e, k

TABLE II

Diethyl Ketone

Liquid at about 30°C		Solid at about −170°C Present authors
Kohlrausch and Köppl	Present authors	
228 (0) e		95 (3b) k ?
342 (½) e, c		
408 (3b) k, e, c	406 (3b) e, k ; P	417 (1b) e
589 (1) k, f, e		
728 (1)	746 (2b) e, k ; P	786 (1b) e, k
1092 (2b) k, e	786 (2b) e, k ; P	
	950 (1b) e, k ; P	950 (1b) e, k
1155 (0) e	1010 (1b) e, k ; P	
1230 (0) e	1093 (4) e, k ; P	1005 (0b) e, k
	1238 (2) k ; P	1095 (1) e, k
1418 (4b) k, e	1271 (0) k ?	
1457 (4b) k, e	1418 (2b) e, k } $\rho > 0.5$	1418 (1b)
	1460 (3b) e, k } $< 6/7$	1460 (1) e, k
1710 ± 8 (4b) f, e	1706 (5b) e ; P	1702 (1) e
2670 (0) k		
2800 (5b) k		2890 (0b) k
2882 (7b) k, i, e	2893 (10b) e, k, q ; P	2920 (2) e, k
2916 (8) k, i, e	2940 (10) e, k, q ; P	2948 (4) e, k
2936 (10b) p, k, i, e	2988 (6) e, k q, $\rho > .5 < 6/7$	2982 (3) e, k, q
2979 (5b) q, p, k, e		

TABLE III

Methyl Ethyl Ketone

Liquid at 30°C		Solid at about −170°C Present authors
Kohlrausch and Köppl	Present authors	
258 (1) e, k	260 (1) e ; D ?	90 (2) k ?
408 (3) e, e, k	401 (3) e, $\rho < 6/7$	
	510 (0) e ?	
592 (3) e, e, f, k	590 (4) e, k ; P	590 (1b) e, k
763 (7) e, e. f, k	760 (8) e, k ; P	770 (2) e, k
812 (0) e		
947 (1b) e, k	950 (1b) e [k] ; P	
1001 (1b) e, k	1002 1b) e, k ; P	
1088 (3) e, k	1090 (4) e, k ; P	1090 (0) e, k
1165 (½) e, k	1170 (3 k ; P	
1247 (½) e, k	1252 (1) k ?	
1412 (3b) e, k	1350 (1) e, k ?	
1450 (3b) e, k	1419 (5) e, k ; D	1416 (1) e, k
	1460 (4) e. k ; D	1460 (0) e
1711 ± 10 (3b) e, f	1705 (6) e ; P	1702 (0b) e
2917 (10b) e, i, k, q	2890 (5) e, k ; P	2896 (1) k
2900 (6b) e, k, p, q	2932 (10b) e, k ; P	2932 (5b) e, k
	2986 (5) e, k ; D	2986 (3) e, k
	3004 (2b) e, k ; D	3000 (1) k

TABLE IV

Di *n*-propyl Ketone

Liquid at about 32°C		Solid at about −170°C Present authors
Kohlrausch and Köppl	Present authors	
305 (5) e, f, k	308 (2) e ; ?	90 (ob) k ?
424 (1b) e		230 (o) e
527 (½) e	520 (ob) e ; ?	308 (o) e
529 (½) e		
626 (½) e		
716 (2) e, k	720 (ob) e, k ; ?	
814 (1) e, k		
866 (2) e, k	870 (ob) e, k ; ?	
914 (4) e, k	914 (1) e, k ; ?	
1037 (3b) e, k	1038 (4d) e, k ; P	1038 (1d)
1114 (3b) e, k	1118 (2) e, k ; P	
1201 (1) e, k	1206 (ob) k ; ?	
1269 (1) e, k	1270 (o) k ; ?	
1288 (1) e, k	1290 (o) k ; ?	
1410 (4b) e, k	1415 (2) e, k ; D	
1443 (7sb) e. k	1458 (5) e, k ; D	1440 (1)
1707 ± 8 (4b) e, f	1705 (5) e ; P	1700 (1)
2735 (2) k	2740 (3) k ; ?	
2875 (12b) e, i, k	2880 (10) e, k ; P	
2913 (10) e, i, k, q	2918 (4d) e, k ; P	2886 (3)
2938 (10) e, i, k, q	2942 (10) e, k ; P	2925 (3)
2966 (9) e, k, q	2974 (5) e, k ; D	2966 (3)

LINES IN THE LOW FREQUENCY REGION

In all these cases a new line at about 95 cm^{-1} on the Stokes side of 4046 A.U. has been observed in the spectrograms due to the solid state. A weak broad band is, however, present exactly in this place in the spectrum of the incident light also. Hence it is difficult to say whether this line is a genuine new Raman line appearing in all these cases. Excitation by 4358 A.U. does not help to solve this question, because there is a strong mercury band at this

distance on the Stokes side of that line also. Careful examination of the spectrogram shows that in the case of diethyl and methyl ethyl ketone there is actually a new line at about 95 cm^{-1} and 90 cm^{-1} respectively superposed on the band observed in the incident spectrum. Hence it can be concluded that there are no new lines of frequencies larger than 38 cm^{-1} in the Raman spectrum of solid acetone, although two lines at 70 and 80 cm^{-1} are observed in the case of solid methyl sulphide. These results are therefore not explained satisfactorily by the hypothesis that these new lines are due to lattice oscillations in which only electrostatic fields take part. Similarly in the case of di-*n*-propyl ketone the band at 95 cm^{-1} is very weak and may be the same band observed in the incident spectrum, but in the spectrogram due to solid ethyl sulphide there is an intense band of frequency 96 cm.$^{-1}$ These results rather indicate that the nature of the new lines in the solid state is somehow dependent upon the presence of some particular atoms in the molecule, *e g*, the sulphur atom in the case of alkyl sulphides and oxygen in the case of ketones. More data, however, are required before such a hypothesis can be substantiated.

CHANGES OBSERVED IN THE LINES DUE TO INTRAMOLECULAR OSCILLATIONS

Acetone.—Before discussing the results obtained in the case of solid acetone we shall first discuss those due to the liquid state in order to find out the symmetry of the molecule in this state. If the two CH_3 groups were rotating freely about the C-C bond the molecule would not possess any symmetry element and all the Raman lines would be polarised. Since some of the lines are found to be totally depolarised the molecule has some elements of symmetry. The number of Raman lines expected in the case of a symmetry C_{2v} is indicated in Table V. It can be seen that eight polarised and sixteen totally depolarised

TABLE V

Acetone $CH_3.CO.CH_3$

C_{2v}	E	C_2	σ_v	σ'_v	n_i	T & R	n'_i	Raman effect.
Γ_1	1	1	1	1	9	1	8	P
Γ_2	1	1	−1	−1	5	1	4	D
Γ_3	1	−1	1	−1	9	2	7	D
Γ_4	1	−1	−1	1	7	2	5	D
U_r	10	2	6	2				
$h_j\chi'_j$	30	−2	6	2				
$h_j\psi_j'$	24	0	6	2				

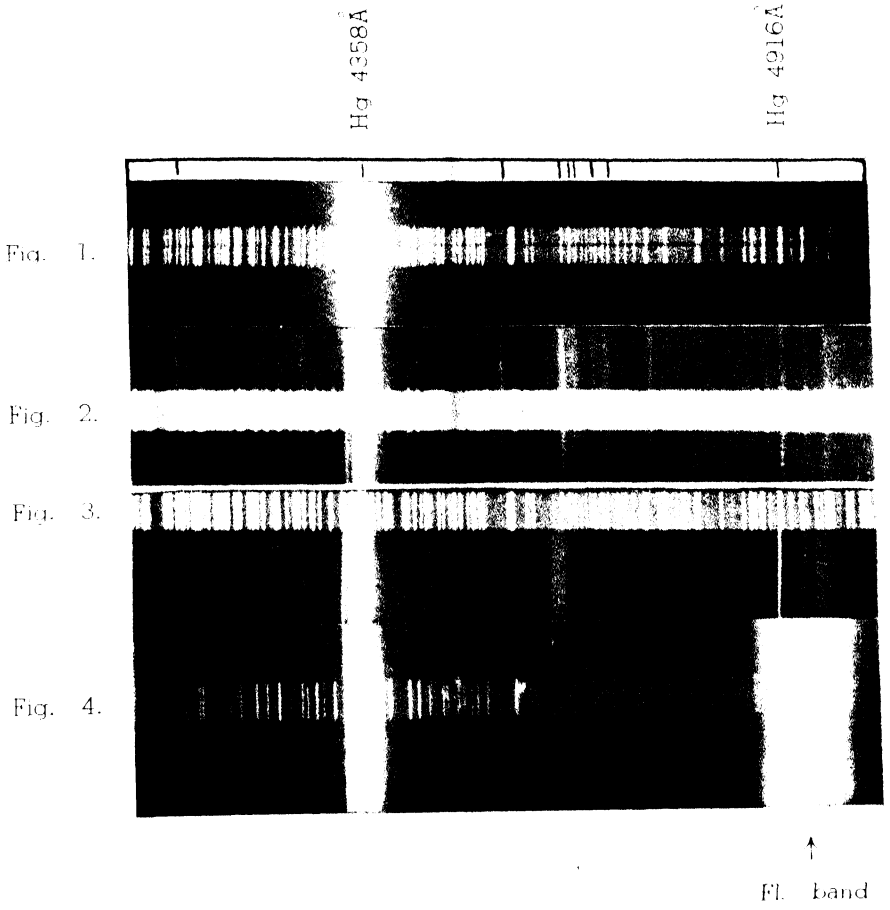
Raman lines are expected in this case. The polarisation was studied previously by Simons (1932) and has been studied by the present authors also. The number

of polarised lines actually observed suggests that the molecule possesses the symmetry C_{2v} in the liquid state and there is no free rotation about the C-C bond.

In the solid state the line 1705 cm^{-1} shifts to 1702 cm^{-1} and is weakened considerably. The line 790 cm^{-1} and the C-H lines 1423 cm^{-1} and 2964 cm^{-1} shift respectively to 800 cm^{-1}, 1430 cm^{-1} and 2976 cm^{-1}. These changes suggest that the molecule is distorted in the solid state. The presence of continuous background due to extraneous light made it difficult to find out whether some of the fainter lines are actually present in the spectrogram due to the solid state or not.

Diethyl ketone.—The results given in Table II show that in the case of diethyl ketone in the liquid state none of the lines is totally depolarised. This shows that the molecule does not possess either any plane of symmetry or a twofold axis of rotation. Although the values of factor of depolarisation of the lines 1418 cm^{-1}, 1460 cm^{-1} and 2988 cm^{-1} are all greater than 0.5 yet they are found to be less than 6/7. In this case also the line 1706 cm^{-1} due to C=O group shifts to 1702 cm^{-1} and diminishes in intensity at the low temperature. The line 2893 cm^{-1} which according to Kohlrausch and Köppl (1934) consists of two lines at 2882 cm^{-1} and 2916 cm^{-1} was not clearly resolved into two components in the spectrogram obtained with the Fuess spectrograph used in the present investigation, but at the low temperature in the solid state this line is split up into two sharp lines 2890 cm^{-1} and 2920 cm^{-1}. As can be seen from Table II the lines 2940 cm^{-1} and 2988 cm^{-1} due to C–H valence oscillations shift to 2948 cm^{-1} and 2982 cm^{-1} respectively in the solid state. In this case all the prominent Raman lines appear in the spectrogram due to the solid state.

Methyl ethyl ketone.—In the case of methyl ethyl ketone although two different groups are attached to the C=O group the molecule possesses a plane of symmetry, because all the lines 1419 cm^{-1}, 1460 cm^{-1}, 2986 cm^{-1} and 3004 cm^{-1} are found to be totally depolarised, in the present investigation. The polarisation of the Raman lines of this substance was also studied previously by Simons (1932) and the line 406 cm^{-1} and these lines except 3004 cm^{-1} which was not resolved in his spectrogram were reported to be totally depolarised. The line 406 cm^{-1}, however, is not observed in the present investigation to be totally depolarised. In this case also the line 1705 cm^{-1} diminishes in intensity in the solid state. Besides this line, the line 1170 cm^{-1} was not clearly visible in the spectrogram due to the solid state owing to the presence of strong continuous background. The hydrogen lines do not undergo much changes in intensity with the solidification of the substance but two of them, *e.g.*, 2890 cm^{-1} and 3004 cm^{-1} shift to 2896 cm^{-1} and 3000 cm^{-1} respectively. Kohlrausch and Köppl (1934) reported only two hydrogen lines 2917 cm^{-1} and 2980 cm^{-1}, probably because these were not resolved into their components by the spectrograph used by them. The changes mentioned above may be due to distortion of the molecules in which the hydrogen atoms are involed.



Raman Spectra.

Fig. 1. : Acetone at about −170°C.
„ 2. : „ „ „ − 30°C.
„ 3. : Di-*n* propylketone − 30°C.
„ 4. : „ „ „ −170°C.

Di-n-propyl ketone.—Most of the Raman lines due to this substance in the liquid state are found to be polarised. As in the case of methyl ethyl ketone some of the hydrogen lines are totally depolarised. Hence the molecule seem to possess a plane of symmetry or twofold axis of rotation. All the Raman lines due to this substance excepting those due to the C-H valence and bending oscillations are very weak. Hence the Raman spectrum due to the solid state obtained in the present investigation is incomplete. The hydrogen lines 2880 cm^{-1}, 2918 cm^{-1}, 2942 cm^{-1} and 2974 cm^{-1} are observed to change to three lines 2886 cm^{-1} 2925 cm^{-1}, and 2966 cm^{-1} in the solid state. The line 1705 cm^{-1} is weakened in the solid state in this case also. These suggest changes in the intermolecular field and probably some distortion of the molecule also in the solid state.

The spectrogram due to the solid di-*n*-propyl ketone at $-170°C$ shows a very intense broad fluorescence band in the region of 4920 A.U. No trace of such fluorescence is observed in the liquid state, as can be seen from Plate II. It has been found that this fluorescence does not appear immediately with the solidification of the substance at about $-32°C$, but it appears only when the solidified mass is further cooled down. At first the fluorescent spectrum consists of a continuous broad band starting from about 4920 A.U. extending upto about 5300 A.U., but when the temperature reaches about $-170°C$ the band becomes stronger and narrower and the maximum occurs at about 4920 cm^{-1}. Another faint band at about 5200 A.U. was visually observed, but it was not recorded in the spectrogram due to insensitivity of the plate in this region. These results were reported briefly in a previous communication (Sirkar and Bishui, 1945). The enhancement of the intensity of feeble fluorescence bands due to impurities at low temperatures is well known, but the results obtained in the present investigation are different from such well known phenomenon in this respect that the spectrogram due to liquid di-*n*-propyl ketone is absolutely free from fluorescence and it is only the strain produced by contraction of the solid at low temperature which gives rise to such a strong fluorescence. The intensity of the fluorescent radiation observed in this case seems to be larger than that of the total scattering, because although extraneous light was present in the scattered light and the spectrum was photographed with a narrow slit of the spectrograph the band is found to be more intense than any of the undisplaced lines.

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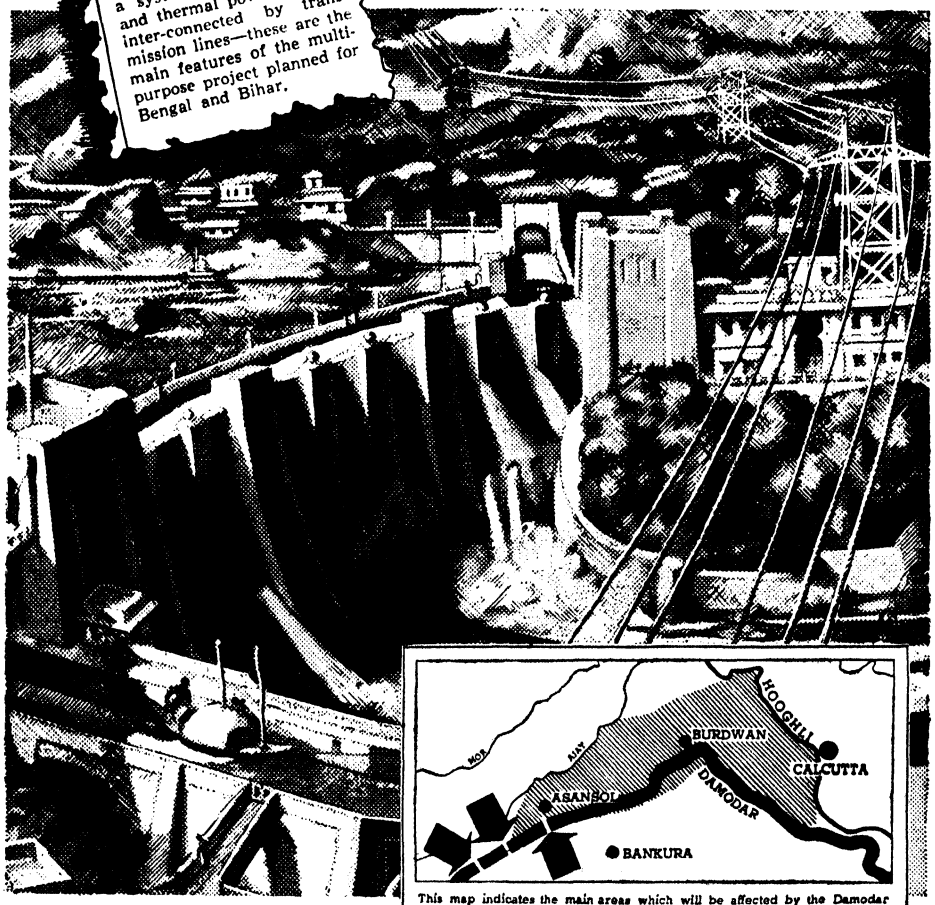

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